A Re-evaluation of Carbon Ring Structure in Coal

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INTRODUCTION

Working models of coal constitution are important because of their potential predictive capacity. A basic approach is to develop a qualitative structure of coal which can be given subsequent quantitative expression. Without a model we are faced, as at present, with the prospect of endless repeat of experiments on all coals of interest. With a working model, however, experimental results on certain coals under certain conditions can in principle be generalized to allow prediction of properties, both physical and chemical, of other coals or the same coals under untested conditions. This is an ultimate objective of developing a working model of coal constitution.

Traditional coal tests provide relatively little insight into structural configuration. Ultimate analysis will yield the elements and their proportions but nothing of their arrangement. The volatiles expelled during carbonization may not have been present as such in the raw coal. They can be formed in situ by primary or secondary reactions. The use of results from such methods for structural analysis, therefore, has always been indirect and inferential.

Direct information on structure, however, is obtainable from X-ray scattering from coals. During such experiments Hirsch (1), for example, found that up to 80% of the carbon is ordered and evidently exists as flat plates or lamellae made up of condensed aromatic rings. By measuring the diameters of the lamellae Hirsch estimated that the number of rings in each lamella was rank dependent varying from 4 or 5 in bituminous coals to 30 or more in anthracite. The remainder of the coal was amorphous to X-rays.

Van Krevelen and co-workers (2) predicted physical and chemical properties from the ultimate analysis. The equations were based on the general equation for alkanes. Ayre and Essenhigh (3) criticize this approach on two grounds: it gives no insight into the structure in coal and prediction of the number of rings in each of Hirsch's lamellae showed considerable discrepancy with experimental values. They, in turn proposed a qualitative model of the coal molecule based on the Hirsch structure and derived an equation relating the number of rings per lamella to the total carbon percentage in the coal. The quantitative expression was based on a relationship previously proposed by Essenhigh (4) between the weight percent oxygen and carbon in coal.

In this present paper the essential features of the Ayre and Essenhigh analysis are used but incorporating an improved relationship between the hydrogen/carbon and oxygen/carbon atomic ratios in coal.

QUALITATIVE MODEL

The structure of coal proposed by Ayre and Essenhigh is an elaboration of that described by Hirsch. The basic unit is considered to be the crystallite which contains all the ordered carbon as condensed aromatic lamellae plus a fixed quantity of amorphous material situated around the edges of the lamellae. The lamella carbon is loosely identified as fixed carbon, and the amorphous material as volatile matter as measured by proximate analysis. Each crystallite may contain a single lamella or groups of two, three, or more lamellae stacked parallel with each other. The amorphous material which is weakly

bonded to the edges of the lamellae, possibly by double or triple bonds, provides for some cross linking between lamellae. A fraction of the amorphous material, however, is considered to be more closely associated with the lamellae than the rest and can be thought of as an integral part thereof, so each lamella contains some hydrogen, oxygen and nitrogen (and possibly sulfur). The coal molecule is thus based on the single lamella with a fixed quantity of associated volatile matter.

According to the X-ray results the percentage of ordered carbon, the number of rings per lamella and the degree of parallel stacking of the lamellae increase with rank. At low carbon percentages the coal is highly porous, the number of rings per lamella is low, and the lamellae are randomly ordered. As the carbon percentage rises the parallel packing of the lamellae improves and both the number of rings per lamella and the fraction of carbon in rings increase. At 89% C what Hirsch described as a perfect "liquid" structure is reached where the crystallite packing is an optimum but a large fraction of the internal pore volume is isolated. A further increase in rank leads to a more rapid increase in the number of rings per lamella and a greater fraction of ordered carbon. At 94% C the structure is almost perfectly graphitic. The changes with rank are illustrated in Figure 1. Coalification is the process of transforming the open structure into the anthracitic structure.

TWO-COMPONENT HYPOTHESIS

Clark and Wheeler (5) identify two main stages of volatile evolution when coal is heated: the constituents easily evolved on heating to 650°C (hydrocarbons, gases, vapors, tars); and, the volatiles less easily evolved on heating above this critical temperature (mainly hydrogen with reduced quantities of carbon bearing materials). The easily evolved volatiles can be considered as being generated from the weakly bonded amorphous material around the edges of the lamellae. The hydrogen rich fraction is evolved as a result of ring coalescence. The two components are thus identified as: the loosely associated amorphous material; and the lamellae of condensed rings and related O and H atoms.

QUANTITATIVE EXPRESSION

Ayre and Essenhigh (3) established first a general equation for the condensed aromatic ring structure. The number of carbon atoms, C_L, in a condensed aromatic structure containing R rings was shown (3) to be given by

$$C_L = 4 + 3R \qquad\qquad 1)$$

and the number of hydrogen atoms H_L for a structure with N double bonds is

$$H_L = 10 + 4R - 2N \qquad\qquad 2)$$

Equations (1) and (2) are based on naphthalane, and assume ring addition so as to minimize carbon atom addition. As an example
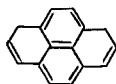
$$
\begin{aligned}
R &= 4, N = 7\\
C_L &= 16\\
H_L &= 12
\end{aligned}
$$

Some of the double bonds may be saturated by hydrogen atoms. If n is the fraction that remain unsaturated

$$
\begin{aligned}
H_L &= 10 + 4R - 2nN\\
&\simeq 10 + 4R - 4n(R-1) \qquad\qquad 3)
\end{aligned}
$$

Equation (3) is an approximate expression rarely in error by more than 2. The hydrogen/carbon ratio in the lamellae is therefore

$$H_L/C_L \quad = \quad [10 + 4n + 4(1-n)R]/(4 + 3R) \tag{4}$$

Oxygen and nitrogen have been omitted from the analysis since their proportions of atoms are small.

WHOLE COAL ANALYSIS

The next step is to express the hydrogen/carbon ratio in the lamellae in terms of measurable quantities. Identifying the lamella carbon as fixed carbon, Ayre and Essenhigh showed that

$$m_H H_L/m_C C_L \quad = \quad (100/C^*)-1 - (O^*/C^*) \tag{5}$$

where C^* and O^* are weight percent carbon and oxygen; and m_H and m_C are molecular weights of hydrogen and carbon. It is not possible to neglect the percentage of oxygen on a weight basis.

To proceed it is necessary to establish relationships between C^*, H^*, and O^*. Since N^* and S^* are usually relatively small we have

$$C^* + H^* + O^* \simeq 100 \tag{6}$$

In addition, an empirical linear relationship between (O/H) [=(O/C)/(H/C)] and (O/C) was established by Essenhigh and Howard (6) that was recently reconfirmed by Yarzab (7) using the Penn State Coal Analysis Data bank. This is illustrated in Fig. 2, noting that the correlation coefficient for the plot was 0.9889. The further relationship that follows is

$$H^*/C^* \quad = \quad A(O^*/C^*)/[1 + B(O^*/C^*)] \tag{7}$$

where A and B are empirical constants with: A = 1/(intercept of Fig. 2); and B = (slope of Fig. 2/intercept of Fig. 2).

In using such data there is often concern expressed that these are whole coal analyses which ignores maceral constituents. As illustrated in Fig. 3, however, Kessler (8) has shown recently, on a somewhat similar plot, that maceral analyses lie on an essentially common band, thus justifying the use of whole coal analyses as in Eq. (7).

It is now possible to solve for O^*/C^* as a function of C^*. The relationship between the number of rings per lamella, R and the total carbon percentage, C^* is obtained by combining equations (4) and (5)

$$[10 + 4n + 4(1-n)R]/[12(4 + 3R)] \quad = \quad (100/C^*) - 1 - (O^*/C^*) \tag{8}$$

Using equations (6), (7) and (8), the value of R as a function of C^* is illustrated in Figure 4 for various values of n. The best fit line to Hirsch's experimental data is for n = 0.6, suggesting that between half and three quarters of the double bonds remain unbroken.

The molecular weight of the lamellae, M_L is then given by

$$M_L \quad = \quad [100\, m_C\, (4 + 3R)]/C^* \tag{9}$$

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and is shown in Figure 5 for the case n = 0.6. Also, the molecular weight of the coal "molecule", M is given by

$$M = M_L \ C*/C_L* \qquad\qquad\qquad 10)$$

and is shown in Figure 5, using for values of C_L* the fixed carbon percentages from Hirsch's original data. The minimum in the whole coal molecular weight is a little unexpected. Walker (9) has suggested it represents the increasing contributions of the greater oxygen percentage in the lignites.

DISCUSSION

Figure 4 shows that the predicted behavior parallels the experimental trends. In particular, choosing n = 0.6, agreement between prediction and experiment is respectable good. Below about 80% carbon the value of R is constant, and tends to infinity at 100% carbon. This can be explained by considering the process of coalification. The rise in the carbon percentage as coalification proceeds can only occur if a fraction of the primary coal material is eliminated (by coalification as a long term chemical reaction). It is reasonable to assume that the fraction that remains is reorganized so that, as proposed by Ayre and Essenhigh (3)

            primary coal material → lamella + material eliminated.

If this is so, raw coal will consist of the lamella with its closely associated fraction of hydrogen, carbon, and nitrogen plus some unchanged parent material. If the unchanged parent material is identified as the amorphous material surrounding the lamellae, then this material contains all the volatile carbon. A plot of fixed carbon versus volatile carbon (Figure 6) is indicative of the growth of lamellae at the expense of the parent material. At about 90% fixed carbon the parent material has run out so that coalification can only continue at the expense of the lamellae, which coalesce. This is consistent with Horton's (10) two stage theory of coalification.

As the number of lamellae increases, the proportion of associated parent material will drop so the molecular weight of the coal molecule will drop slightly as the carbon percentage increases. At about 90% carbon, however, ring coalescence occurs and the molecular weight will rise rapidly. These tends are illustrated in Figure 5.

The model is intended, of course, as a first step in a full model of coal structure. It is clearly lacking in that nitrogen and sulfur are missing. It is also not yet able to predict the degree of detail on pyrolysis described, for example, by Suuberg et al (11). The initial agreement between theory and the X-ray results of experiment, however, is encouraging and suggests that the model is probably adequate as a framework or skeleton for further developments.

SUMMARY

1. X-ray data suggest that the coal molecule may be viewed in terms of a lamella of condensed aromatic rings of carbon plus a fraction of loosely associated volatile matter.

2. The model described is in agreement with the X-ray data, showing that the number of rings per lamella is constant at 4 or 5 up to about 90% carbon above which it rapidly rises with rank.

3. The model shows that the molecular weight of the coal molecule drops slightly as the carbon percentage rises to 90% above which it rises rapidly with rank.

4. The lamella carbon is identified as the fixed carbon and the amorphous material as the volatile matter as determined by the proximate analysis.

5. The model is consistent with the Two-Component Hypothesis of coal constitution (5) and the Two-Stage Theory of coalification (10).

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4. Essenhigh, R.H., Fuel, 34, 497 (1955).

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8. Kessler, M.F., Fuel, 52, 191 (1973).

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11. Suuberg, E.M., Peters, W.A. and Howard, J.B., American Chemical Society Fuels Division Preprints, 22 (1), 112 (1977).
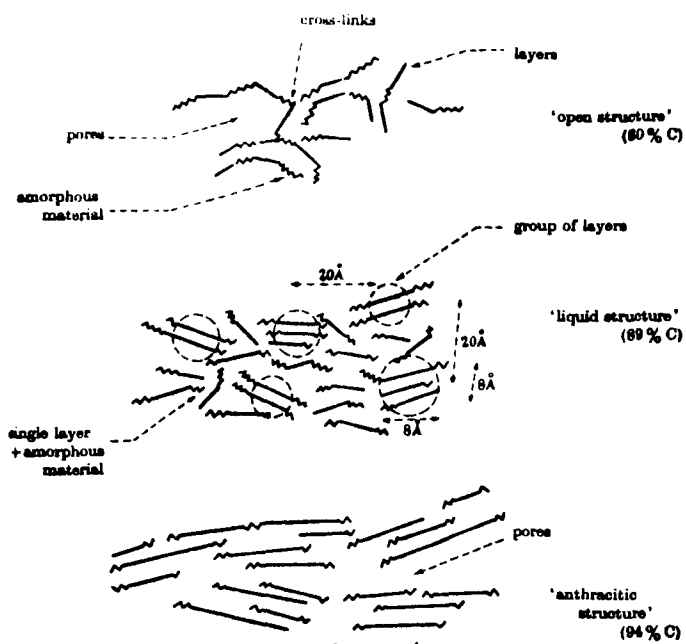
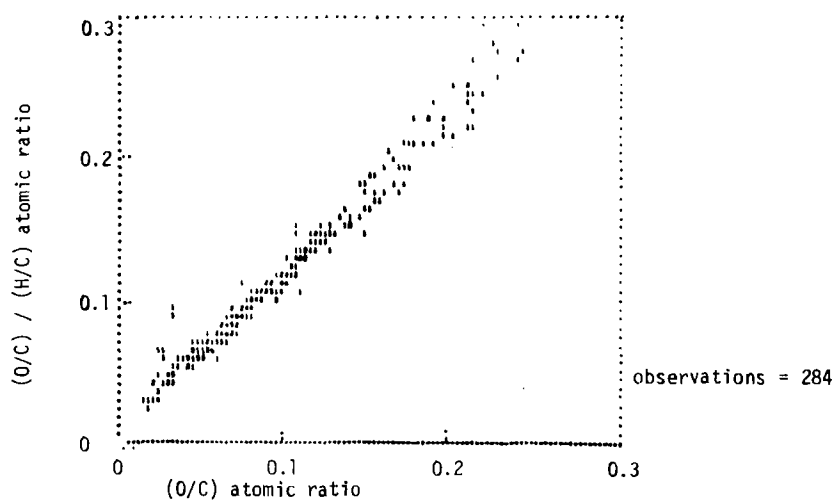Figure 1 - Coal Structure as a Function of Rank
(source: Hirsch (1))

Figure 2 - Variation of (O/C) / (H/C) with (O/C) atomic ratios
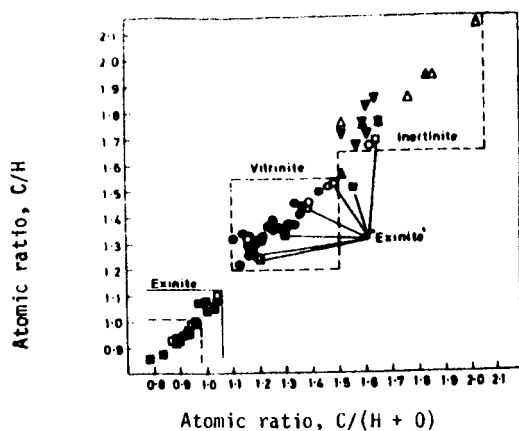for various coals. (Source: Yarzab, (7)).

Figure 3 - Variation of C/H ratio with C/(H + O) ratio
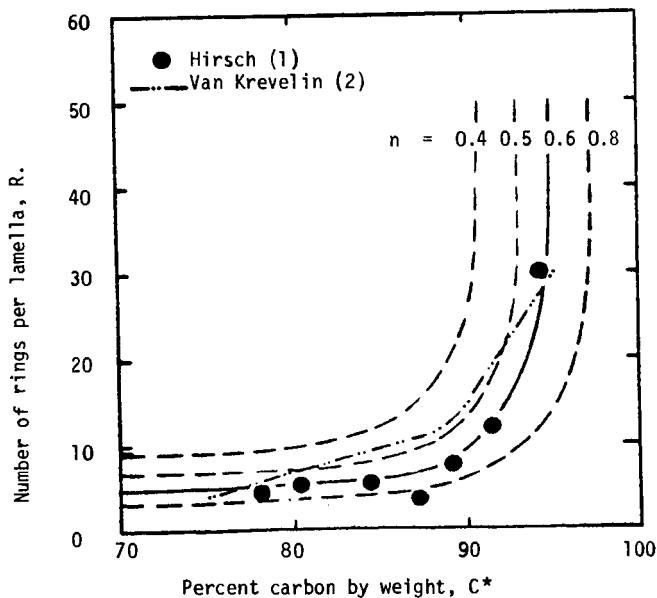for various macerals. (Source: Kessler, (8))

Figure 4 - Variation of number of rings per lamella with
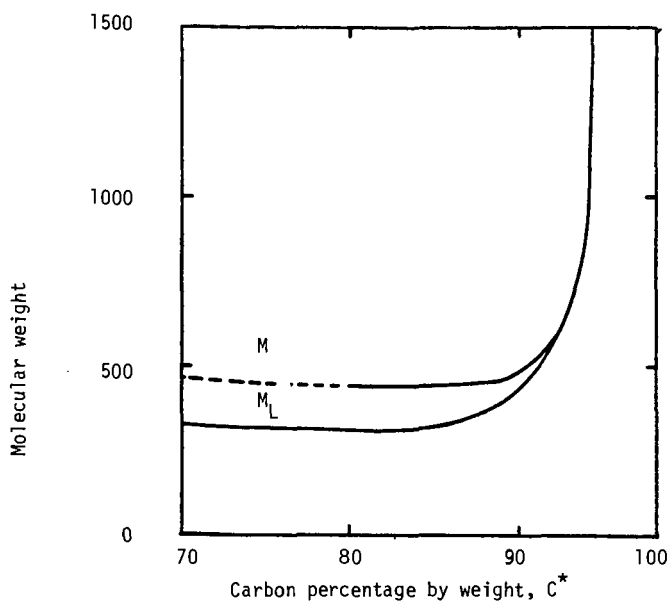carbon percentage by weight.

Figure 5 - Variation of molecular weight of lamella and coal
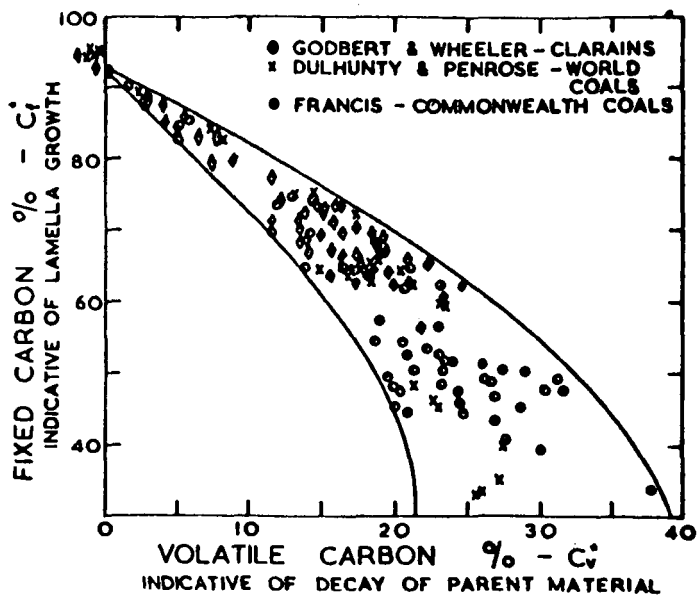molecule with weight percent carbon.

Figure 6 - Relation between lamella growth and decay of parent
material. (Source: Ayre and Essenhigh, (3))